AD 682586

TRANSLATION NO. 565

DATE: 1955

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FEB 27 1969

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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

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PHASE REVERSAL IN EMULSIONS

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The mechanism of phase reversal in emulsions is generally atributed to the necessity for the transformation of a hydrophilic into an oleophilic stabilizer, or conversely. However, the reversal of o/w type emulsions into the w/o type occurs under the influence of univalent cations, which do not affect the surface-active properties of the typical stabilizers for direct emulsions ─ the alkali soaps [1].

A much closer approach may be made to a s 'ution of this problem by a consideration of the results of our systematic study of direct and reverse emulsions of maximum concentration [2]. It was found that to determine the possibility of formation of an emulsion of a given type it is insufficient to have information concerning the hydrophilic or oleophilic nature of the stabilizer with respect to two immiscible pure liquids (the model case). In general, the type of the stable emulsion formed is determined by the properties of the liquids in contact within it, one of which may be, for example, an aqueous salt solution. A stable emulsion is formed when a continuous adsorptional-solvation layer is produced on the outer surface of the droplets, and for this, according to the independent surface action principle, one of the liquids in the emulsion shou' predominately solvate either the polar or the nonpolar portions of the stabilizer molecules. In the case of two pure liquids ─ water and benzene ─ the molecules of alkali soap adsorbed on the droplet surfaces are ensured considerable hydration of the polar groups by water. The thickness of the solvation layers then predominates on the water side, and o/w type emulsion is stabilized. Electrolytes in sufficient concentration dehydrate the polar groups of the soap molecules, which leads to predominate solvation of the hydrocarbon chains of the soap molecules and their independent surface action. In these conditions emulsions of the w/o type are stabilized.

If this is so, no difficulties are presented by phase reversal in direct and reverse concentrated emulsions by setting up in them some given concentration of alkali cations of the same nature as the soap cations. The following experiments were performed for this purpose. By shaking in a cylinder, a stable emulsion of the o/w type, containing equal volumes of benzene and aqueous soap solution, was obtained. Dry salt was then added to the emulsion, after which the emulsion was again shaken till the salt dissolved completely. The advantage of using dry electrolyte instead of an aqueous solution is that its action increases gradually and comparatively regularly as solution proceeds. On the other hand, addition of a concentrated salt solution leads to the formation of clots of the salted-out soap, which are difficult to disperse, and makes reproducible results difficult to obtain. The type of emulsion was determined microscopically by dyeing with Sudan III, and also by dilution of the emulsions by water and benzene.

In a large series of experiments, the following was invariably observed. As the salt concentration increases, an emulsion of the o/w type becomes increasingly unstable, and at a critical concentration of electrolyte it is usually destroyed and separates into two layers. Further increase of the salt content leads to the formation of first an unstable and then a fully stable emulsion of the w/o type. The reversed emulsion, in turn, can easily be converted into the original stable emulsion of the o/w type, if aqueous solution of the stabilizer is added to it with shaking. In these experiments the aqueous solution lowers the electrolyte concentration below the critical value, which causes phase reversal.

Tables 1 and 2 give some results of experiments with emulsions stabilized by aqueous solutions of sodium oleate.

The phases are reversed similarly in emulsions with ammonium and triethanolamine oleates. Table 3 gives the critical values of concentrations of salts, which precede phase reversal, at which the emulsions are destroyed or become very unstable.

These results show that the critical concentration of salts in phase reversal has a practically constant value (0.25-0.3 mole/l) which does not depend on the nature of the added electrolyte or the properties of the stabilizer. The same salt concentration is maintained also at different contents of the stabilizer in the aqueous solution. For example, in the concentration range from 0.1 to 0.5 mole/l for aqueous solutions of sodium oleate, the critical concentration of NaCl in our experiments was 0.25-0.28 mole/l.

On turning to data on stabilization of concentrated emulsions of the w/o type by alkali soaps [3] we see that at the salt concentrations indicated above, ∼ 50% of the stabilizer is salted out of the aqueous solution, after which,

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TABLE 1

Reversal of Emulsion Phases by Means of NaCl. Concentration of Sodium Oleate ~0.3 mole/l

Concentration of NaCl in mole/l	Emulsion type	Stability of emulsion
0.08	o/w	Stable
0.17	o/w	Unstable
0.25	—	Destroyed
0.34	w/o	Unstable
0.42*	w/o	Stable
0.34*	w/o	Unstable
0.25*	—	Destroyed
0.17*	o/w	Unstable
0.14*	o/w	Stable

* Decrease of salt concentration by supplementary addition of soap solution.

TABLE 2

Reversal of Emulsion Phases by Means of Na_2SO_4. Concentration of Sodium Oleate ~0.3 mole/l

Concentration of Na_2SO_4 in mole/l	Emulsion type	Stability of emulsion
0.11	o/w	Stable
0.15	o/w	Stable
0.18	o/w	Unstable
0.26	—	Destroyed
0.28	w/o	Unstable
0.31	w/o	Unstable
0.35*	w/o	Stable
0.28*	w/o	Unstable
0.25*	w/o	Unstable
0.22*	—	Destroyed
0.14*	o/w	Unstable
0.10*	o/w	Stable

* Decrease of salt concentration by supplementary addition of soap solution.

on further increase of electrolyte concentration, conditions are created for the formation of a reverse emulsion. At concentrations of electrolyte below the critical, at which the degree of salting-out of the soap is still insufficient, direct emulsions are still stabilized. Thus, electrolytes have an effect of the same type on emulsions of any concentration. When, then, determines the emulsion type in our experiments? We base our answer to this question on the fact that one of the main purposes of the stabilizer is a substantial increase of the cohesion between unlike liquids with the aid of diphilic surface-active molecules, the polar and nonpolar portions of which are simultaneously and independently solvated at the interphase surface by the disperse phase and the dispersion medium of the emulsion. As was shown by our study of direct and reverse emulsions of maximum concentration [2], the degree of solvation of the polar groups by the aqueous phase and of the hydrocarbon chains of the stabilizer molecules by the nonaqueous phase, is not the same, corresponding to different values of δ_{crit} for the adsorption-solvation layers on the droplets. By means of one solvation layer a close interaction between the adsorbed molecules of the stabilizer and the droplets is effected, and a second solvation layer on the side of the dispersion medium prevents coalescence of the droplets.

TABLE 3

Critical Salt Concentrations in mole/l in Phase Reversal

$(NH_4)_2CO_3$	$(NH_4)_2SO_4$	NH_4Cl	NaCl	Na_2CO_3	Na_2SO_4
Ammonium oleate, concentration 0.3 mole/l					
0.24	0.26	0.24-- 0.28	—	—	—
Triethanolamine oleate, concentration 0.3 mole/l					
0.26	0.23	0.24	0.29	0.24	0.26

When a soap, for example sodium oleate, is dissolved in water, the latter hydrates the carboxyl groups of the soap molecules, and the thickness of this portion of the whole protective layer is $\delta'_{crit} = 0.01\ \mu$ [4]. The hydrocarbon chains, solvated by benzene, form the second part of the protective layer, the thickness of which was also measured and is $\delta''_{crit} = 0.006\ \mu$ [4]. The ratio γ between the thicknesses of the adsorption-solvation layers at the interphase surface is the deciding factor in the stabilization of an emulsion of a given type. In the present case, for sodium oleate

$$\gamma = \frac{\delta'_{crit}}{\delta''_{crit}} > 1$$

and the disperse phase is benzene, which solvates the hydrocarbon chains to a smaller extent than the polar groups are hydrated by water.

By the use of aqueous salt solutions the hydration of the polar groups is sharply decreased, and the adsorption-solvation portion of the protective layer on the water side will have a thickness of the order of several molecular diameters, i.e., it will not be capable of stabilizing oil droplets. It is in these conditions that the thickness of the adsorption-solvation part of the protective layer on the benzene side predominates, and a water-in-oil emulsion is formed, because

$$\gamma = \frac{\delta'_{crit}}{\delta''_{crit}} < 1.$$

Thus, the emulsion type is determined by the ratio of the thicknesses of the adsorption-solvation layers on the two sides of the separation boundary between unlike liquids, and this ratio can serve as a quantitative measure of the solvation of the stabilizer.

TABLE 4

Values of γ and Types of Emulsion

Oleates	Liquids		Critical layer thickness		γ	Emulsion type
	1	2	δ'_{crit}, μ	δ''_{crit}, μ		
Sodium	Water	Benzene	0.01	0.006	>1	o/w
	Salt solutions	Benzene	→0	0.006	<1	w/o
Ammonium	Water	Benzene	0.007	0.003	>1	o/w
	Salt solutions	Benzene	→0	0.003-0.005	<1	w/o
Triethanolamine	Water	Benzene	0.01	0.002	>1	o/w
	Salt solutions	Benzene	→0	0.002-0.012	<1	w/o

The above may be formulated as follows: the dispersion medium of an emulsion is the one which, out of two immiscible pure liquids or solutions, forms the thicker adsorption-solvation continuous coating at the droplet surfaces either with the polar or with the nonpolar portions of the molecules (particles) of the stabilizer. This is supported by our experimental data on the stabilization of direct and reverse emulsions [2], as is shown in Table 4.

SUMMARY

1. Phase reversal with the aid of univalent cations has been studied in emulsions stabilized by alkali oleates.

2. It was established that the critical concentration of salts, which precedes phase reversal, is a practically constant value, which does not depend on the properties and the concentration of soap, or on the nature of the electrolyte added, with a cation common with the soap.

3. It was proved that conversion of o/w to w/o emulsions takes place when the solvation of the hydrocarbon chains of the stabilizer molecules exceeds the hydration of the polar groups. When hydration of polar groups predominates, conversion of w/o to o/w emulsions takes place.

LITERATURE CITED

[1] H. V. Tartar, et. al., J. Phys. chem., 33, 435, 1929; 34, 373, 1930; 34, 379, 1930.

[2] L. Ya. Kremnev, Trans. Leningrad Chem. Tech. Inst., No. 3, 63, 1936; L. Ya. Kremnev and T. P. Papkova-Kvitsel, Trans. Leningrad Chem. Tech. Inst., No. 3, 77, 1936; L. Ya. Kremnev and Yu. G. Khasina, Trans. Leningrad Chem. Tech. Inst., No. 7, 93, 1939; L. Ya. Kremnev and S. A. Soskin, J. Gen. Chem., 16, 2004 (1946); Colloid J., 9, 269 (1947); L. Ya. Kremnev and R. N. Kagan, Colloid J., 10, 436 (1948); L. Ya. Kremnev and Yu. G. Shteinberg, Trans. Leningrad Chem. Tech. Inst., 17, 63, 1950; L. Ya. Kremnev and N. I. Kuibina, Colloid J., 13, 39 (1951).

[3] L. Ya. Kremnev and N. I. Kuibina, Colloid J., 16, 358 (1954).*

[4] L. Ya. Kremnev and S. A. Soskin, Colloid J., 9, 269 (1947); L. Ya. Kremnev and N. I. Kuibina, Colloid J., 16, 358 (1954).*

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